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## **FLUIDIZED BED STEAM REFORMING OF ORGANIC AND NITRATE CONTAINING SALT SUPERNATE (U)**

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# **FLUIDIZED BED STEAM REFORMING (FBSR) OF ORGANIC AND NITRATE CONTAINING SALT SUPERNATE**

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## **ABSTRACT**

A salt supernate waste (Tank 48H) generated at the Savannah River Site (SRS) during demonstration of In Tank Precipitation (ITP) process for Cs removal contains nitrates, nitrites, and sodium tetraphenyl borate (NaTPB). This slurry must be pre-processed in order to reduce the impacts of the nitrate and organic species on subsequent vitrification in the Defense Waste Processing Facility (DWPF). Fluidized Bed Steam Reforming (FBSR) is a candidate technology for destroying the nitrates, nitrites, and organics (NaTPB) prior to melting. Bench scale tests were designed and conducted at the Savannah River National Laboratory (SRNL) to demonstrate that bench scale testing can adequately reproduce the CO/CO<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O fugacities representative of the FBSR process and form the appropriate product phases. Carbonate and silicate product phases that were compatible with DWPF vitrification were achieved in the bench scale testing and test parameters were optimized for a pilot scale FBSR demonstration.

## **INTRODUCTION**

An In Tank Precipitation (ITP) technology was developed at the SRS to remove Cs<sup>137</sup> from high level waste (HLW) supernates. During the ITP process monosodium titanate (MST) and sodium tetraphenylborate (NaTPB) were added to the salt supernate to adsorb Sr<sup>90</sup>/Pu<sup>238</sup> and precipitate Cs<sup>137</sup> as CsTPB, respectively. This process was demonstrated at the SRS in 1983. The demonstration produced 53,000 gallons of 2.5 wt% Cs rich precipitate containing TPB, which was later washed and diluted to 250,000 gallons. This material is currently stored in SRS Tank 48H. The washed precipitate was to ultimately be disposed in borosilicate glass in the Defense Waste Processing Facility (DWPF).

Due to safety concerns, the ITP process was abandoned in 1998, and new technologies are being researched for Cs<sup>137</sup> removal. In order to make space in the SRS Tank farm, the Tank 48H waste must be removed. Therefore, the Tank 48H waste must be processed to reduce or eliminate levels of nitrates, nitrites, and NaTPB in order to reduce impacts of these species before vitrification at the DWPF. Fluidized Bed Steam Reforming (FBSR) is being considered as a candidate technology for destroying the nitrates and the NaTPB prior to melting.

The FBSR technology is capable of destroying the organic sodium, potassium, cesium tetraphenyl borate phases, e.g. NaTPB, KTPB, and CsTPB, at moderate temperature and converting the organic phases to (Na,K,Cs)<sub>2</sub>O or (Na,K,Cs)<sub>2</sub>CO<sub>3</sub> or (Na,K,Cs)SiO<sub>3</sub>, CO<sub>2</sub> gas, and H<sub>2</sub>O in the form of steam [1,2]. The high nitrate and nitrite content of the Tank 48H slurry will be converted to N<sub>2</sub> thereby minimizing NO<sub>x</sub> emissions during processing. Any organics are oxidized to CO<sub>2</sub> instead of CO during processing. The FBSR can be electrically heated (pilot scale units) or operated in an auto-thermal mode, whereby the energy needs are supplied by the incoming superheated steam and by the oxidation of organics from the waste and carbon reductants. For production scale units, auto-thermal steam reforming is the preferred mode of operation. Since there is no open flame as in incineration and since the product emissions are CO<sub>2</sub> and N<sub>2</sub> instead of CO and NO<sub>x</sub>, the FBSR process is Clean Air Act and Maximum

Achievable Concentration Technology (MACT) compliant. The solid oxide or mineral phases produced, e.g.  $(\text{Na,K,Cs})_2\text{O}$ ,  $(\text{Na,K,Cs})_2\text{CO}_3$ , or  $(\text{Na,K,Cs})\text{SiO}_3$ , are considered compatible with subsequent processing to borosilicate glass in the Defense Waste Processing Facility (DWPF) because their melting temperatures are  $<1050^\circ\text{C}$  and this should not create any melt rate related impacts.

The objectives of the current study were to demonstrate the following with a Tank 48H simulant:

- destruction of TPB with the FBSR process operating between  $650\text{--}725^\circ\text{C}$
- destruction of nitrate at  $>99\%$  with addition of sugar as a reductant
- destruction of antifoam with the FBSR process operating between  $650\text{--}725^\circ\text{C}$
- formation of  $\text{Na}_2\text{CO}_3$  FBSR product to be compatible with mixing the FBSR product into a DWPF feed tank for subsequent vitrification
- formation of a  $\text{Na}_2\text{SiO}_3$  or  $\text{Na}_4\text{SiO}_4$  FBSR product to be compatible with mixing the FBSR product into a DWPF feed tank or as an addition to the Slurry Mix Evaporator (SME) in place of a portion of the frit
- assessment of the melting temperature of the  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SiO}_3$  FBSR products to evaluate impacts (if any) on melt rate
- optimization of the amount of reductant to ensure that excess reductant was not contained in the FBSR product that would alter the carefully controlled REDuction/OXidation (REDOX) equilibrium in the DWPF melter [3]
- optimization of test parameters for subsequent pilot scale testing of Tank 48H simulant at Idaho National Engineering and Environmental Laboratory (INEEL)
- demonstration that bench scale studies can duplicate the complex reactions in the FBSR process

## BACKGROUND

Studsvik built and tested a commercial Low-Level Radioactive Waste (LLRW) FBSR Processing Facility in Erwin, TN, in 1999 [4]. In January 2000, commercial operation commenced [1]. The Studsvik Processing Facility (SPF) has the capability to process a wide variety of solid and liquid LLRW streams including: ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions with contact radiation levels of up to  $100\text{R/hr}$ . The licensed and heavily shielded SPF can receive and process liquid and solid LLRWs with high water and/or organic content.

The Erwin facility employs the THERmal Organic Reduction (THOR<sup>sm</sup>) process, developed by Studsvik, which utilizes pyrolysis\*/steam reforming technology. THOR<sup>sm</sup> reliably and safely processes a wide variety of LLRWs in the unique, moderate temperature ( $\sim 700^\circ\text{C}$ ), dual-stage, pyrolysis/reforming, fluidized bed treatment system. The reforming process has demonstrated effectiveness in volatilizing/combusting organics and separating sulfur and halogens from inorganic waste materials. Of special relevance is the capability of the THOR<sup>sm</sup> technology to convert nitrates to nitrogen and sodium salts to sodium compounds that are suitable for direct disposal and/or subsequent vitrification.

In February 2002, THOR<sup>sm</sup> demonstrated the capability of producing sodium aluminosilicate waste forms for Hanford's sodium-bearing low activity waste (LAW) [2]. Other demonstrations performed by Hazen showed that LAW waste could be transformed into  $\text{Na}_2\text{CO}_3$ ,  $\text{NaAlO}_2$ , or

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\* Pyrolysis chemically decomposes organic materials by heat in the absence of oxygen.

Na<sub>2</sub>SiO<sub>3</sub> feed material for the LAW Hanford melter. Addition of no solid co-reactant yields a sodium carbonate product. Sodium combines with carbon dioxide in the reformer gases to provide a sodium carbonate product. Addition of a Al(OH)<sub>3</sub> co-reactant will provide an NaAlO<sub>2</sub> product, addition of SiO<sub>2</sub> will provide an Na<sub>2</sub>SiO<sub>3</sub> product. Addition of kaolin clay will provide an NaAlSiO<sub>4</sub> product. The latter has been shown to perform well as a final waste form [2,5].

In November 2002, THOR<sup>sm</sup> was contracted to demonstrate the FBSR technology to produce a carbonate waste solid for Idaho National Engineering and Environmental Laboratory's acidic and radioactive Sodium-Bearing Waste (SBW) [6]. This demonstration successfully converted the SBW to a Na<sub>2</sub>CO<sub>3</sub> product that met the Waste Isolation Pilot Plant (WIPP) Waste Acceptance Criteria (WAC) for transuranic (TRU) waste. During the demonstration, data were collected to determine the nature and characteristics of the product, the operability of the technology, the composition of the off-gases, and the fate of key radionuclides (cesium and technetium) and volatile mercury compounds. The product contained a significant fraction of elemental carbon residues. Mercury was quantitatively stripped from the product but cesium, rhenium (Tc surrogate), and the heavy metals were retained. Nitrates were not detected in the product and NO<sub>x</sub> destruction exceeded 98% [6]. The steam reformer off-gas was monitored and it was determined that no O<sub>2</sub> was present. The off-gas was mostly (76%) H<sub>2</sub>O (wet, N<sub>2</sub>-free basis). CO levels averaged 1.3%, while the measured CH<sub>4</sub> levels averaged 0.1%.

In the THOR<sup>sm</sup> FBSR process, a granular/particle bed material is fluidized with low pressure superheated steam. The lower zone of the fluid bed is operated in strongly reducing conditions to facilitate reduction of nitrates and nitrites to nitrogen gas. The upper zone of the fluid bed is operated under oxidizing condition by injection of oxygen. The oxidizing zone converts residual carbon reductants and organics into carbon dioxide and water vapor. The fluidized bed material can include ceramic media and/or reformed product granules. The incoming waste feed coats the fluidized particles and is instantly dried. The large active surface of dried nitrates readily reacts with the hot carbon reductant particles, carbon monoxide and hydrogen gases, and the reduced metal and metal oxides particles in the fluidized bed. Hydrogen and CO are formed when the steam oxidizes any solid carbon material (Equation 1) or any intermediate hydrocarbons (Equation 2). The CO in the gaseous mixture resulting from Equation 1 and Equation 2 can be made to react with more water vapor in the water gas shift reaction (WGSR) as shown in Equation 3. These reactions are important sources of heat that facilitate the dehydration, denitration, and reaction of the waste plus additive mixtures.



Free hydrogen promotes radical generation and chain reaction propagation in the reformer bed. A significant benefit of the FBSR process is that it produces zero-liquid releases. All water is released as water vapor.

## EXPERIMENTAL

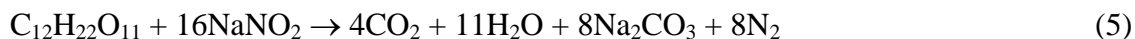
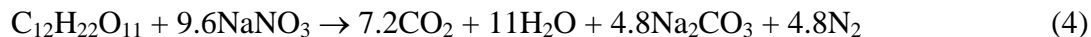
A simulant of the Tank 48H solution was prepared according to Table I. This slurry has approximately 13.7 wt% solids. Antifoam (IIT Corp. B52) was added at 100 ppm antifoam per wt% solids [7]. Five wt% Fe<sub>2</sub>O<sub>3</sub> was added as Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O to provide an indicator of the REDUction/OXidation (REDOX) equilibrium that the sample experienced in sealed crucibles inside the oven. Having ~5 wt% Fe<sub>2</sub>O<sub>3</sub> present enabled the Fe<sup>+2</sup>/ΣFe ratio of the solid product sample to be measured from which the oxygen fugacity,  $\log f_{O_2}$ ,  $\log p_{H_2O} / p_{H_2}$ , and  $\log p_{CO_2} / p_{CO}$  of the reactions inside the sealed crucibles could be determined. All samples were analyzed for Fe<sup>+2</sup>/ΣFe analysis by the Baumann method [8].

Table I. Tank 48H Simulant Recipe

Species	M/L
NaTPB	0.0728
NaOH	1.8425
NaNO <sub>2</sub>	0.4709
NaNO <sub>3</sub>	0.2753
Na <sub>2</sub> CO <sub>3</sub>	0.1295
NaAlO <sub>2</sub>	0.1118
Na <sub>2</sub> SO <sub>4</sub>	0.0071
Na <sub>3</sub> PO <sub>4</sub>	0.0077
NaCl	0.0088
NaF	0.0059
KNO <sub>3</sub>	0.0779

The T48H simulants were batched into stainless steel beakers. The slurry was carbonated with dry ice to convert the NaOH to Na<sub>2</sub>CO<sub>3</sub> until a pH of ~9.5 was reached. This “acidification” from pH 13.3 to 9.5 also minimized foaming of the slurry. This ensured that once the carbonated material was put into a sealed crucible that a CO<sub>2</sub> atmosphere would be maintained. This served to duplicate the control of the atmosphere in the FBSR with CO<sub>2</sub> gas.

The reductant of choice was sucrose. A test matrix (Table II) was developed that varied three different levels of reductant based on the following stoichiometric equations:



Where the stoichiometric ratio of [C]:[N] for nitrate species is 12/9.6=1.25 (Equation 4) and 12/16=0.75 for nitrite species (Equation 5).

Three different levels of sucrose (none, ½X stoichiometric, and 1X stoichiometric) and three different reaction times (1/2 hour, 3 hours, and 48 hours) were tested. High purity (99.999%) Al<sub>2</sub>O<sub>3</sub> crucibles were used to simulate Al<sub>2</sub>O<sub>3</sub> bed material and to determine if the FBSR product was adhering to the simulated bed media. Temperatures of 650°C and 725°C were tested to see which levels of reductant optimized the WGSR (Equation 3) at which temperatures.

The known melt temperature of alumina containing FBSR products are >1280°C [9,10]. Hence, the lower melting Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SiO<sub>3</sub> FBSR products were targeted for study. Since

the feed was already carbonated, nothing needed to be added to the samples to optimize the  $\text{Na}_2\text{CO}_3$  product. Precipitated silica was added to the tests where the desired final FBSR product was  $\text{Na}_2\text{SiO}_3$  or  $\text{Na}_4\text{SiO}_4$ .

The carbonated slurries were dried to peanut butter consistency to ensure that some  $\text{H}_2\text{O}$  remained in the sample to create steam for the WGSR. Alumina crucibles were sealed with nepheline ( $\text{NaAlSiO}_4$ ) gel that melts at a temperature lower than the test temperature. This prevents air inleakage during reaction but allows other gases to escape by slow diffusion through the gel. The sealed samples were placed in a calibrated furnace at the test temperature designated in the test matrix. This generated a combined atmosphere of steam, CO from decomposition of the sucrose and  $\text{CO}_2$  thus duplicating the WGSR species (Equation 3). The furnace was purged with 99.99% Ar to ensure that no  $\text{O}_2$  mixed with any  $\text{H}_2$  or CO escaped through the crucible seal.

Samples were analyzed by X-ray diffraction (XRD) to determine if the desired FBSR product was achieved. Samples were measured by High Pressure Liquid Chromatography (HPLC) to determine if the TPB was adequately destroyed by the FBSR reactions. Analyses were also conducted to determine if any secondary TPB reaction products were present, e.g 3PB and 2PB. Total carbon (TC), Total Inorganic Carbon (TIC), and Total Organic Carbon (TOC) were also analyzed.

Samples were measured by Ion Chromatography (IC) for  $\text{NO}_2$ ,  $\text{NO}_3$ , F, Cl and  $\text{SO}_4$  to determine the fate of these anions and the percent nitrate destruction. For those samples that the desired FBSR product was a silicate, samples were dissolved using a  $\text{LiBO}_2$  fusion and the solution analyzed by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) for Na, K, and Si to determine if the correct ratios of silica additive had been achieved during experimentation. Differential Thermal Analysis (DTA) was performed on selected products to determine the melting temperature. Details of all the analyses performed are given elsewhere [11].

## DISCUSSION

### Baseline Testing

A sample (T48-0) was tested as a baseline. The T48-0 sample was carbonated, anitfoam and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were added, and the sample was dried at  $60^\circ\text{C}$ . This sample was analyzed for TPB, anions, TC, TIC, TOC and REDOX as a baseline case (see Table III). These analyses demonstrated that there was 95,100 ug/g of TPB (Table III) present in the samples after the carbonation and drying steps. The presence of the TPB was also confirmed by the measurement of TOC, which showed 19,500 ug/g of organic carbon. Either the TPB or the anitfoam (an organic) may have reacted with the  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  because an all  $\text{Fe}^{+3}$  dried solution should have had a REDOX measurement of  $\sim 0$  and the measurement was 0.44. This indicated that a considerable amount of  $\text{Fe}^{+2}$  was present or that the organics interfered with the REDOX measurement. Anion analysis of the base case indicated  $<100$  ug/g of  $\text{NO}_2$  and 163,000 ug/g or 16.3 wt% of  $\text{NO}_3$ . This number was used with the measured  $\text{NO}_3$  data [11] to calculate the  $\text{NO}_3$  destruction values given in Table III.

### Tetraphenylborate Destruction

Samples were tested at two different temperatures,  $650^\circ\text{C}$  and  $725^\circ\text{C}$  (Table II). Tetraphenylborate (TPB) was completely destroyed in all the samples tested, i.e., the TPB, 2PB and 3PB were all  $<5$  ug/g indicating that the thermal treatment destroyed all the TPB and its derivatives. This was confirmed by the TOC analyses for all the samples thermally treated when

<100 ug/g of TOC was observed. This indicates that FBSR is a viable technology for destruction of the organics in Tank 48H.

#### Carbonate FBSR Products

For all of the FBSR samples in which the desired product was  $\text{Na}_2\text{CO}_3$  (samples T48-1 through T48-5B and T48-13), analysis by XRD indicated that a mixture of  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  was formed regardless of temperature and residence time in the furnace (Table II and Table III). However, for the T48-13 sample that was heated at  $650^\circ\text{C}$  for 48 hours, the XRD analysis indicated no minor constituents. This meant that the minor constituents that had appeared in the same sample reacted for only 3 hours were due to incomplete reaction. Test T48-5B or T48-13 appeared optimal for making the  $\text{Na}_2\text{CO}_3$  FBSR product at  $650^\circ\text{C}$  with 1X stoichiometric sugar and 3-48 hour residence time, as no minor phases were identified as incomplete reactants. Only the two primary phases,  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , were present in the T48-5B and T48-13 samples.

#### Silicate FBSR Products

In the current study  $\text{Na}_4\text{SiO}_4$  was chosen as the FBSR phase of choice because it melts at  $\sim 1120^\circ\text{C}$  and can only coexist with a liquid phase down to temperatures as low as  $1040^\circ\text{C}$ . This choice was made to limit any potential liquid phase in the steam reformer that might cause bed agglomeration.  $\text{Na}_2\text{SiO}_3$  may be acceptable for use as feed in the DWPF as its melting temperature is  $\sim 1080^\circ\text{C}$  but it can coexist with a  $\text{Na}_2\text{O}-\text{SiO}_2$  liquid phase that melts as low as  $825^\circ\text{C}$  and may cause FBSR bed agglomeration. Sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) was the silicate FBSR product phase made by THOR<sup>sm</sup> in their pilot scale studies with Hanford's high  $\text{Na}^+$  containing Low Activity Waste (LAW).

For all of the simulated FBSR samples in which the desired product was  $\text{Na}_4\text{SiO}_4$  with a  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of 2:1 (T48-6 through T48-12), a potassium aluminosilicate zeolite phase known as faujesite ( $\text{K}_{48.2}\text{Al}_{48.2}\text{Si}_{143.8}\text{O}_{384} \cdot 243\text{H}_2\text{O}$ ) was identified by XRD and a sodium silicate of a 1:1  $\text{Na}_2\text{O}:\text{SiO}_2$  stoichiometry had formed (Table III). Excess  $\text{SiO}_2$  does not appear on the XRD pattern since the precipitated  $\text{SiO}_2$  that was added to the sample is amorphous and will not give an XRD pattern. It was apparent that the faujesite was consuming some of the  $\text{SiO}_2$  that was meant to form the 2:1 sodium silicate phase.

Subsequent testing (T48-14) was designed to compensate for the silica being consumed by the faujesite. X-ray Diffraction analysis (Table III) again indicated that the major phases in the T48-14 sample after a 48 hour residence time were still the faujesite and the 1:1  $\text{Na}_2\text{O}:\text{SiO}_2$  phase. Analysis of all the silicate FBSR products was performed to determine if the correct ratios of  $\text{Na}_2\text{O}:\text{SiO}_2$  had been added during experimentation. These analyses indicated that some of the  $\text{Na}_2\text{O}:\text{SiO}_2$  ratios measured were biased low by  $\sim 20\%$ . This may be because the precipitated silica contains absorbed water and the exact amount of the absorbed water had not been measured.

In summary, if a silicate FBSR phase was desired, a silica FBSR phase was the major phase formed. Although the exact  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of the desired FBSR silicate phase was never achieved due to incomplete reaction and silica deficient starting mixtures, this would not hinder the usage of any sodium silicate FBSR material made from Tank 48H slurry in DWPF.

#### Nitrate and Sugar Destruction

In the sample test matrix (Table II), samples with the designation of B indicate comparison of tests at the two different reaction temperatures. These were designed into the test matrix to test the optimum  $\text{NO}_x$  destruction at the various temperatures, e.g. optimize the WGSR. Hence



samples T48-2B, 5B, 7B and 10B were tested at 650°C, while samples T48-2, 5, 7, and 10 were tested at 725°C.

For two of the pairs of samples tested at the different temperatures, T48-2 and 2B and T48-5 and 5B, the desired FBSR product was  $\text{Na}_2\text{CO}_3$ . Samples T48-2 and T48-2B had no sugar and samples T48-5 and T48-5B had 1X stoichiometric sugar. Comparison of the XRD spectra of the two tests without sugar demonstrates that the FBSR products in absence of sugar includes un-decomposed  $\text{NaNO}_3$  which indicates that nitrate destruction is incomplete when sugar is absent at 650°C and 725°C. This was confirmed by nitrate analyses [11]. For the sample pair T48-5 and T48-5B sucrose was present at 1X stoichiometry. These samples had 99.1% and 97.5%  $\text{NO}_3$  destruction at the 650°C and 725°C temperatures respectively (Table III). This indicates that the WGSR may be better optimized at 650°C than at the 725°C. Likewise, the TOC analyses [11] indicated no residual TOC in the form of sucrose in the samples and the XRD spectra did not indicate any residual  $\text{NaNO}_3$  (Table III).

For two of the pairs of samples tested at the different temperatures, T48-7 and 7B and T48-10 and 10B, the desired FBSR product was a sodium silicate. Sample T48-7B had no sugar and Sample T48-10B had 1X stoichiometric sugar. Comparison of the XRD spectra of the two tests without sugar did not show any un-decomposed  $\text{NaNO}_3$  but the nitrate analyses [11] indicated that considerable  $\text{NO}_3$  remained in the samples without sugar. The nitrate destruction percentages given in Table III for these samples indicate that nitrate was only partially destroyed at either temperature for samples T48-7 and T48-7B. For the sample pair T48-10 and T48-10B sucrose was present at 1X stoichiometry. These samples had 98.7% and 94.1%  $\text{NO}_3$  destruction (Table III). This again indicates that the WGSR may be better optimized at 650°C than at the 725°C. Likewise, the TOC analyses [11] indicated no residual TOC in the form of sucrose in the samples and the XRD spectra did not indicate any residual  $\text{NaNO}_3$  (Table III).

The small amount of TOC measured in all the samples [11] indicated that at  $\frac{1}{2}$  to 1X sugar stoichiometry that most of the sugar added is consumed during denitration and that the FBSR product should not be overly reducing and thus compatible with DWPF processing of the FBSR product.

#### Particle Agglomeration to Simulated $\text{Al}_2\text{O}_3$ Bed Material

No adherence of the silicate or carbonate phases onto the  $\text{Al}_2\text{O}_3$  crucibles was noted in any of the tests. Therefore, if the FBSR bed media used is  $\text{Al}_2\text{O}_3$  there should not be any particle agglomeration with the bed material regardless of whether the FBSR product is carbonate or silicate. This also indicates that the  $\text{Na}_2\text{SiO}_3$  phase that was produced most often as an FBSR product in this study appears to be an acceptable FBSR product phase in that it did not preferentially melt and react with the  $\text{Al}_2\text{O}_3$  crucible.

#### FBSR Product Melt Temperatures

FBSR product samples T48-5B ( $\text{Na}_2\text{CO}_3$  made at 650°C), T48-10 (mixed  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SiO}_3$  and faujesite), and T48-11 ( $\text{Na}_2\text{SiO}_3$  and faujesite) were measured by Differential Thermal Analysis (DTA) to determine their melting temperature. The melt temperatures were 980°C, 1022°C, and 1049°C, respectively. These melt temperatures are all compatible with melting of these phases in the DWPF.

#### REDOX Measurements and the Water Gas Shift Reaction (WGSR)

Because the FBSR product is a mixture of oxide species, the Electro-Motive Force (EMF) REDOX series developed for DWPF glasses [12] was used to calculate the  $\log f_{\text{O}_2}$  from the measured REDOX of the FBSR product [11]. Published correlations [13] between  $-\log f_{\text{O}_2}$ ,

temperature,  $\log p_{H_2O} / p_{H_2}$ , and  $\log p_{CO_2} / p_{CO}$  allows the  $\log p_{H_2O} / p_{H_2}$  and  $\log p_{CO_2} / p_{CO}$  to be determined for the atmosphere achieved in the sealed crucibles. The  $\log p_{H_2O} / p_{H_2}$  and  $\log p_{CO_2} / p_{CO}$  are the partial pressures of the two half reactions for the WGSR given in Equation 3. The average REDOX ratio for the FBSR samples tested at 725°C and 650°C show that  $\log f_{O_2}$  values of -9.69 and -10.75, were achieved respectively. These negative  $\log f_{O_2}$  values mean that no oxygen was present during the FBSR reactions. The  $\log f_{O_2}$  can be converted to  $\log p_{H_2O} / p_{H_2}$  and/or  $\log p_{CO_2} / p_{CO}$ . The  $\log p_{H_2O} / p_{H_2}$  in the FBSR crucibles were between +5 and +6. The  $\log p_{CO_2} / p_{CO}$  in the FBSR crucible studies were in the range of +4.5 to +5. The positive values for  $\log p_{H_2O} / p_{H_2}$  and  $\log p_{CO_2} / p_{CO}$  indicate that the conditions of the WGSR were adequately simulated.

#### Volumes of FBSR Product For DWPF

The 250,000 gallons of T48H slurry should make ~29,470 gallons of solid FBSR  $Na_2SiO_3$  solid product or ~26,246 gallons of solid FBSR  $Na_2CO_3$  solid product for subsequent treatment in the DWPF. This calculation used a measured FBSR product density of 1.46 g/cc [6]. It is calculated that 25,500 gallons of FBSR product (almost all of T48) could be added to the next 500,000 gallon DWPF sludge batch (at 18 wt% solids) if ~7 wt%  $Na_2O$  from the FBSR product is substituted for 7 wt%  $Na_2O$  in a given DWPF frit as done previously [14].

Table II Simulated T48H Steam Reformer Optimization Matrix

Test ID	Temp (°C)	Time (Hours)	Sugar Stoichiometry	Addition	Phase(s) Desired
T48-0	25	0	0	0	$Na_2CO_3$
T48-1	725	½	0	0	$Na_2CO_3$
T48-2	725	3	0	0	$Na_2CO_3$
T48-2B	650	3	0	0	$Na_2CO_3$
T48-3	725	3	½	0	$Na_2CO_3$
T48-4	725	½	1	0	$Na_2CO_3$
T48-5	725	3	1	0	$Na_2CO_3$
T48-5B	650	3	1	0	$Na_2CO_3$
T48-6	725	½	0	$SiO_2$	$Na_4SiO_4$
T48-7	725	3	0	$SiO_2$	$Na_4SiO_4$
T48-7B	650	3	0	$SiO_2$	$Na_4SiO_4$
T48-8	725	3	½	$SiO_2$	$Na_4SiO_4$
T48-9	725	½	1	$SiO_2$	$Na_4SiO_4$
T48-10	725	3	1	$SiO_2$	$Na_4SiO_4$
T48-10B	650	3	1	$SiO_2$	$Na_4SiO_4$
T48-11	725	48	0	$SiO_2$	$Na_4SiO_4$
T48-12	725	48	1	$SiO_2$	$Na_4SiO_4$
T48-13	650	48	1	0	$Na_2CO_3$
T48-14	725	48	1	$SiO_2$	$Na_4SiO_4$ + faujesite
T48-15	725	48	1	$SiO_2$	$Na_2SiO_3$ + faujesite

Table III Simulated T48H Steam Reformer Analytic Results

Test #	Major Phase Desired	Major Phases Identified by X-Ray Diffraction	Minor Phases Identified by X-Ray Diffraction	NaTPB, 3PB, 2PB (ug/g)	Percent NO <sub>x</sub> Destroyed
T48-0	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> H(CO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> , Na(NO <sub>3</sub> ), NaNO <sub>2</sub> , Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O	Na <sub>2</sub> SiO <sub>3</sub> , KAl(SO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>12</sub>	95,100 <5,<5	0
T48-1	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	Al(OH) <sub>3</sub> (?), Ca <sub>8</sub> Al <sub>2</sub> Fe <sub>2</sub> O <sub>12</sub> CO <sub>3</sub> (OH) <sub>2</sub> •22H <sub>2</sub> O	<5,<5,<5	30.1
T48-2	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	Al(OH) <sub>3</sub> (?), Ca <sub>8</sub> Al <sub>2</sub> Fe <sub>2</sub> O <sub>12</sub> CO <sub>3</sub> (OH) <sub>2</sub> •22H <sub>2</sub> O	<5,<5,<5	4.3
T48-2B	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	Al(OH) <sub>3</sub> (?), NaNO <sub>3</sub> , Ca <sub>8</sub> Al <sub>2</sub> Fe <sub>2</sub> O <sub>12</sub> CO <sub>3</sub> (OH) <sub>2</sub> •22H <sub>2</sub> O	<5,<5,<5	24.5
T48-3	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	Ca <sub>8</sub> Al <sub>2</sub> Fe <sub>2</sub> O <sub>12</sub> CO <sub>3</sub> (OH) <sub>2</sub> •22H <sub>2</sub> O	<5,<5,<5	99.5
T48-4	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	Ca <sub>2</sub> SiO <sub>4</sub> (?), Al(OH) <sub>3</sub> (?)	<5,<5,<5	98.1
T48-5	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	Ca <sub>8</sub> Al <sub>2</sub> Fe <sub>2</sub> O <sub>12</sub> CO <sub>3</sub> (OH) <sub>2</sub> •22H <sub>2</sub> O Al(OH) <sub>3</sub> (?)	<5,<5,<5	97.5
T48-5B	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	NONE	<5,<5,<5	99.1
T48-6	Na <sub>4</sub> SiO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, K <sub>48.2</sub> Al <sub>48.2</sub> Si <sub>143.8</sub> O <sub>384</sub> •243H <sub>2</sub> O	Na <sub>2</sub> SiO <sub>3</sub>	<5,<5,<5	35.0
T48-7	Na <sub>4</sub> SiO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> SiO <sub>3</sub> , Na <sub>7.89</sub> (AlSiO <sub>4</sub> ) <sub>6</sub> (NO <sub>3</sub> ) <sub>1.92</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O NaTPB (?)	<5,<5,<5	63.3
T48-7B	Na <sub>4</sub> SiO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> SiO <sub>3</sub> , Na <sub>7.89</sub> (AlSiO <sub>4</sub> ) <sub>6</sub> (NO <sub>3</sub> ) <sub>1.92</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, K <sub>48.2</sub> Al <sub>48.2</sub> Si <sub>143.8</sub> O <sub>384</sub> •243H <sub>2</sub> O	<5,<5,<5	41.4
T48-8	Na <sub>4</sub> SiO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> SiO <sub>3</sub>	KAlSiO <sub>4</sub> , K <sub>48.2</sub> Al <sub>48.2</sub> Si <sub>143.8</sub> O <sub>384</sub> •243H <sub>2</sub> O	<5,<5,<5	95.2
T48-9	Na <sub>4</sub> SiO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> SiO <sub>3</sub> , K <sub>48.2</sub> Al <sub>48.2</sub> Si <sub>143.8</sub> O <sub>384</sub> •243H <sub>2</sub> O	KAlSiO <sub>4</sub>	<5,<5,<5	92.8
T48-10	Na <sub>4</sub> SiO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> SiO <sub>3</sub> , K <sub>48.2</sub> Al <sub>48.2</sub> Si <sub>143.8</sub> O <sub>384</sub> •243H <sub>2</sub> O	NONE	<5,<5,<5	98.7
T48-10B	Na <sub>4</sub> SiO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> SiO <sub>3</sub> , K <sub>48.2</sub> Al <sub>48.2</sub> Si <sub>143.8</sub> O <sub>384</sub> •243H <sub>2</sub> O	KAlSiO <sub>4</sub>	<5,<5,<5	94.1
T48-11 (see 6)	Na <sub>4</sub> SiO <sub>4</sub>	Na <sub>2</sub> SiO <sub>3</sub> , K <sub>48.2</sub> Al <sub>48.2</sub> Si <sub>143.8</sub> O <sub>384</sub> •243H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O	<5,<5,<5	99.8
T48-12 (see 10)	Na <sub>4</sub> SiO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O Na <sub>2</sub> SiO <sub>3</sub>	NONE	<5,<5,<5	98.8
T48-13 (see 5B)	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	NONE	<5,<5,<5	99.0
T48-14	Na <sub>4</sub> SiO <sub>4</sub> fauesite	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> SiO <sub>3</sub>	Na(NO <sub>3</sub> )	<5,<5,<5	98.5
T48-15	Na <sub>2</sub> SiO <sub>3</sub> fauesite	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> SiO <sub>3</sub> , Na(NO <sub>3</sub> ) K <sub>48.2</sub> Al <sub>48.2</sub> Si <sub>143.8</sub> O <sub>384</sub> •243H <sub>2</sub> O	<5,<5,<5	99.4

## CONCLUSIONS

The purposes of the current study, organic destruction and downstream processing of T48H waste slurry, were fulfilled as documented by the following:

- TPB was destroyed in all 19 samples tested with the simulated FBSR process at operational temperatures 650-725°C; 650°C seemed to optimize the NO<sub>3</sub> destruction
- >99% destruction of nitrate was achieved with addition of sugar as a reductant at 1X stoichiometry and TOC analyses indicated that excess reductant was not present in the FBSR product which ensures that the REDuction/OXidation (REDOX) equilibrium of the DWPF melter would not be adversely impacted
- destruction of anitfoam was also achieved at operating temperatures between 650-725°C based on measured TOC
- for all tests in which Na<sub>2</sub>CO<sub>3</sub> was the desired FBSR product phase, Na<sub>2</sub>CO<sub>3</sub> was produced, which has been shown to be compatible with the DWPF melt process as it melted at 980°C as measured by DTA
- for all tests in which Na<sub>4</sub>SiO<sub>4</sub> or Na<sub>2</sub>SiO<sub>3</sub> was the desired FBSR product a mixture of sodium silicates
  - this was determined to be a problem with water absorption by the SiO<sub>2</sub> additives used and the consumption of SiO<sub>2</sub> by a potassium aluminate zeolite (faugessite) that formed
  - formation of a sodium silicate (mixed with Na<sub>2</sub>CO<sub>3</sub> or alone) is compatible with mixing the FBSR product into a DWPF feed tank or as an addition to the Slurry Mix Evaporator (SME) in place of some of the DWPF glass forming frit because the mixtures melted at temperatures of 1022°C and 1049°C, respectively, as measured by DTA
- the recommended test parameters for pilot scale testing of Tank 48H simulant at Idaho National Engineering and Environmental Laboratory (INEEL) were given by samples T48-5B and T48-14
- the sealed crucible studies demonstrated that bench scale studies can duplicate the complex reactions, especially the Water Gas Shift Reactions, and the associated  $\log p_{H_2O} / p_{H_2}$  and  $\log p_{CO_2} / p_{CO}$  atmospheres in the FBSR process.

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